

An Exclusive Analysis of Cation Exchange Capacity(CEC) of the Soil Using Cohex Method

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ABSTRACT

The essential features of soil are brought to light by the Cation Exchange capacity Measurements. This study mainly focuses on analyzing the results related to the three standardized methods for finding out the Cation exchange capacity (CEC) and Exchangeable cations in the soils based on three different exchange reagents which are Cobalt hexamine(cohex)trichloride, barium chloride and ammonium acetate. Like the reagents, the exchange procedure namely single extraction, successive extraction that are followed, illustrate to be entirely different. The values when compared and calculated with barium and cohex as index cations show the uniformity. These two methods can be termed equivalent. Ammonium acetate, which buffers the pH of the extracts, results in the differences in the proportion of negatively charged sites, particularly those linked with organic matter. This results in large differences from CEC values brought out with the remaining two methods. Compared to barium chloride method, cohex method is quite practicable and it possesses good repeatability. The soil is distinguished with more correctness with regard to cohex method than the barium chloride method.

Keywords: Cation exchange capacity (CEC) / cobalt hexamine (cohex) trichloride.

INTRODUCTION

For the purpose of measuring the Cation exchange capacity (CEC) of soils, many methods are already in practice (Chapman, 1965 Rhoades, 1982). The CEC value we got is the outcome of a specific state of equanimity between the test sample and the given environment. It comprises a reagent and the chosen experimental condition. The great variation in the ionic strength of the reagent solution or the pH of the suspension is apparent (Morais *et al.*, 1976; Gillman *et al.*, 1983).

The cohex with its simple octahedral structure is often coated as the suitable example for describing the concomitant roles of the s, p and d orbitals in chemical transition metals (Gray, 1969). The stable cohex swaps very easily and puts forward satisfactorily and accurate results with little reagent excess through it is relatively large (its ionic radius is 0.323nm according to Morel, 1957).

The possibility of exactness with the measurements of CEC is obtained with cohex chloride which is an unbuffered reagent. An added advantage of cohex chloride is that it can be used in solution at low concentration ($0.0166 \text{ mol.L}^{-1}$) since these conditions come close to natural soil condition (Guadalix *et al.*, 1988). In three different procedures like single extraction, successive extraction (NF ISO 11260) Cohex chloride is used and they have been already followed and examined. The aim of this article is to analyse and compare the methods by using three electrolytes namely cohex chloride, barium chloride and ammonium acetate.

MATERIAL AND METHOD

Soil Samples

Collection of Soil samples has been done in various parts of Chennai in Tamilnadu, India, Around fifteen samples were selected from the surface horizon of each cultivated soil and the samples were air dried and examined with the standardized methods.

Methods

The ammonium acetate method

Metson proposed this Ammonium acetate method in 1956. Subsequently, it is extensively used all over the world. This method had undergone many changes and adaptations as suggested in France by Lefevre (1961). As described in the French standard AFNOR NFX 31-130.

Accordingly, a percolation of a 1 mol.L^{-1} ammonium acetate solution ($\sim 75 \text{ ml}$) through a test portion of 2.5g of soil has been taken by the ammonium saturation of the exchange sites. As a result the excess reagent is carried out with several rinsing with ethanol ($\sim 75 \text{ ml}$). The solid phase then after drying in air is agitated in 50 ml of a 1 mol.L^{-1} solution of a sodium chloride. The spectrophotometry measures the exchanged ammonium. It also provides the measurement of CEC.

This is followed by a single extraction of 2.5g of sample in 50ml of a molar solution of ammonium acetate in which the cations are currently measured instantly. The AFNOR NFX 31-108 standard includes such procedure.

The Barium chloride method

It was in 1979 that Gillman proposed this method for the first time. Later Gillman and sumpter, 1986, changed the same. Furthermore it was tested and it underwent many implementations after it was standardized in 1994. The same later is explained and referred to by ISO 11260. With 30ml of 0.1 mol.L⁻¹ BaCl₂ solution with 2.5g of test portion is shaken (1h) and tested. A centrifugation separates the solid and liquid phases. This operation is repeated two times. Then the three supernatants are collected. They are then used for the purpose of determining the exchanged cation. The soil with 30ml of 0.0025 mol.L⁻¹ BaCl₂ is equilibrated and the solid portion is shaken again. But the next time the same process prolongs with 30ml of 0.02mol.L⁻¹ magnesium sulphate (mgso₄) solution. (initially the shaking time was 2h but in the last time it has done overnight). Because of this, the barium exchange with magnesium is absorbed and then it precipitated in the form of BaSO₄. The dreg of the content is then determined by flame atomic absorption spectrometry. It is then subtracted from the formal content. This difference in CEC values are noted down.

The cobalt hexamine chloride (Cohex) method

A previous study by ciesielski and sterckeman, 1997 describes procedure for operation. It forms our basic reference. It points out that by simply shaking the test portion in the reagent the exchange is carried out. For 100ml reagent, the quantity of test portion weighed (2.5g). The sufficient concentration of cohex ions remaining in

solution, this is a concentration found out by spectrophotometry without any chemical pretreatment of the solution. The cohex loss from solution gives the CEC of the sample. The flame atomic absorption spectrometry measures the Ca and Mg and the flame atomic emission spectrometer for exchangeable cation contents.

RESULTS AND DISCUSSION

Through comparing different methods, the particular behavior among the tested samples can be brought to light. These tested samples show that the reactions caused by the extractants may vary, based on the soil characteristics. On the other hand, the compared methods are termed equivalent when closer linear correlations are observed. Perceptively, we note a clear difference between two kinds of equivalent: A metrological equivalence and physico-chemical equivalence. The previous one is relative to the measured quantities called interchangeability. Ciesielski and Sterckeman (1997) have already explained the requirements required to meet each kind of equivalence and the identical conditions espoused in the present work. The ammonium acetate (Buffered reagent) method is not equivalent to the cohex chloride (Unbuffered reagent) method due to a large range of their pH values. Ammonium acetate provokes a higher pH in acid soil suspensions, thus causing an increase in the negatively charged sites of organic matter. Barium Chloride extracts larger quantities of cations ($A_{BaCl_2} > 1$) but for all the parameters, the comparison of the cohex chloride, the amount of cations extracted and determination coefficients are then lower for Barium Chloride as compared with cohex

chloride ($A_{1\text{cohex}} > A_{\text{bacl2}}$). This brings out that fact that the yield of exchange reaction of cohex chloride is more compared to other two methods.

Cohex-single Extraction

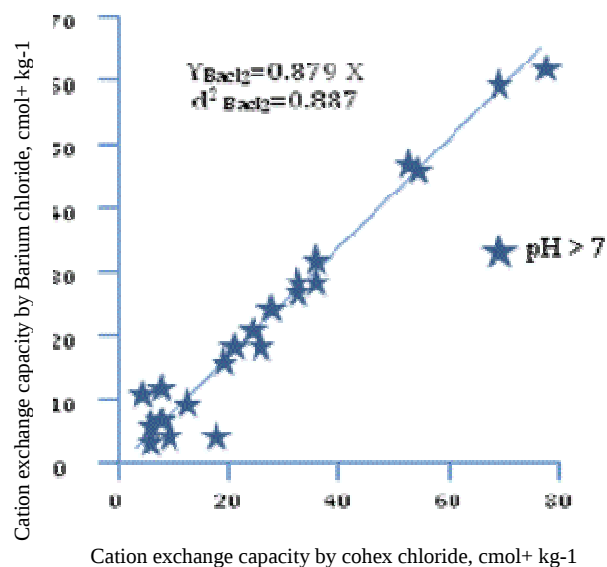
The volume of the reagent 100ml with a concentration of cohex is of $5\text{cmol} \cdot \text{L}^{-1}$ has been taken with 5g of test sample (soil). The suspension was shaken for 2h at

20°C , and then it has been filtered with low filtration speed filter paper. With this method the exchange is achieved and the operating conditions chosen (Orsini and Remy: 1976). The sample masses of 2g, 2.5g, 3g were used to extend the ranges between 2.5, 5, 30 and $80.5\text{ cmol} \cdot \text{kg}^{-1}$ respectively. Direct spectrophotometry provides better repeatability of the measurement.

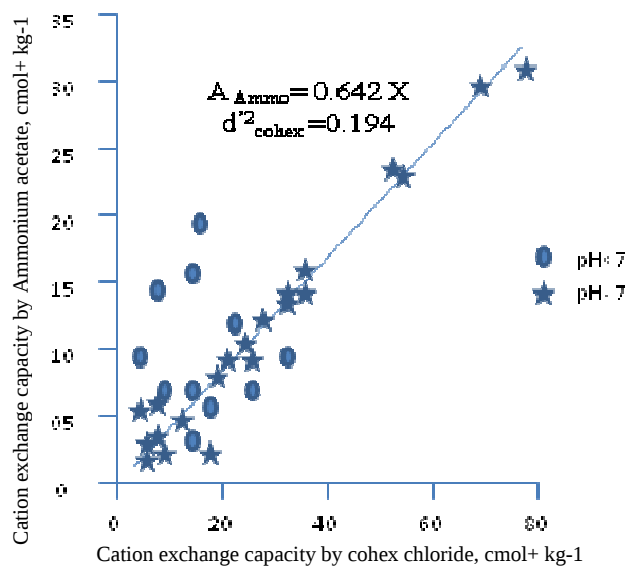
Comparison of cation exchange capacity (CEC) and exchangeable cations obtained from cohex chloride and barium chloride methods.

Units	All Soils	Calcium		Magnesium		Potassium	
	CEC Cmol Kg^{-1}	Acid Soils Cmol Kg^{-1}	All Soils CEC	Acid Soils Cmol Kg^{-1}	All Soils CEC	Acid Soils Cmol Kg^{-1}	All Soils CEC
K1	0.879	1.067	1.142	1.062	1.112	1.187	1.197
	0.887	0.862	0.829	0.893	0.865	0.884	0.859
K2	1.112	1.129	1.107	1.132	1.001	1.229	1.136
	0.892	0.843	0.812	0.889	0.852	0.887	0.847

- $K1 = Y_{\text{BaCl2}} = A_{\text{BaCl2}} * Y_{\text{single}} : K2 = Y_{\text{Cohex}} = A_{1\text{ Cohex}} * Y_{\text{single}}$
- d^2_{BaCl2} & d'^2_{Cohex} – determination coefficients
- A_{BaCl2} & $A_{1\text{ Cohex}}$ – regression coefficients
- Y_{single} : Cohex single extraction
- Y_{Cohex} successive extractions
- $A_{\text{BaCl2}} = 0.879 : d^2_{\text{BaCl2}} = 0.887$
- $A_{1\text{ Cohex}} = 1.112 : d'^2_{\text{Cohex}} = 0.892$



Relationship between cation exchange capacity (CEC) values obtained with cohex chloride and barium chloride



Relationship between cation exchange capacity (CEC) values obtained with cohex chloride and ammonium acetate method

Cohex – Successive Extractions

The exchange was carried out with 2.5g sample that was taken with 50ml of a solution containing 5 Cmol+L⁻¹cohex ion,

which was shaken for 2h at 20⁰c. This method was repeated twice, thus yielding three extracts, which were mixed together, after pipetting an equal volume of each of them.

Comparison of cation exchange capacity (CEC) and exchangeable cations obtained from cohex chloride and Ammonium acetate methods.

Units	CEC all Soils	Calcium		Magnesium		Potassium	
		Acid soils	CEC All soils	Acid soils	CEC All soils	Acid soils	CEC All soils
A _{ammo}	0.642	1.010	1.124	1.024	1.164	1.179	1.159
d ² _{cohex}	0.194	0.864	0.664	0.872	0.876	0.812	0.811

A_{ammo} : regression coefficients ;

d²_{cohex} : determination coefficients

CONCLUSION

An analysis of the validity of a direct spectrophotometric determination of the cohex ion is done in this study. It also further explains the fact that the repeatability of measurements is improved. The nature of the physiochemical mechanism taken in for study and the magnitude of the incidence on the recorded parameters, especially for calcareous soils with exception of saturation rates appear to be equivalent. This conclusion is the result of the comparison of the different exchange procedure. However this equivalence should never be taken to mean that the methods are mutually changeable with regard to metrological respects. The use of single extraction for routine analysis is recommended eventually after repeated consideration of different

aspects. The scale of the values obtained from the certain level does not basically change with the improvement in the yield of the exchange reaction. These remain comparable besides being a coefficient close to one. For most of the applications, demerits go beyond the suitable interest of a better yield in cases like dissolution of non-exchangeable species or the utilization of more intricate and a lengthy procedure. The CEC value obtained from cohex is highly dependable, precise and optimized when put side by side with the other two methods.

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